Explanation of the Colossal Sensitivity of Silicon Pentaerythritol Tetranitrate (Si-PETN) Explosive

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Supporting Information

Table S1 Comparison of B3LYP and M06 for various bond energies. We conclude that the M06 is more accurate.

O-N BDE	B3LYP	M06	Experiment[6]
Methyl-nitrate	35.5	42.5	41.2±1.0
Ethyl-nitrate	34.1	42.1	41.0±1.0
propyl-nitrate	36.2	44.3	42.3±1.0
Iso-propyl-nitrate	36.0	44.2	41.1±1.0
C-O BDE	B3LYP	M06	Experiment
Methyl-nitrate	75.0	83.6	81.0±1.0

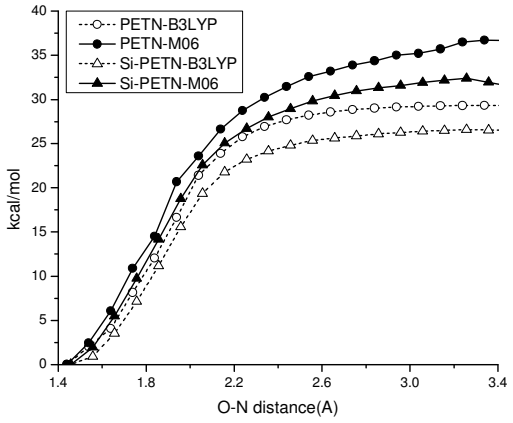

Figure S1. The O-N bond length scan by B3LYP and M06 at 6311G** level. Zero point energies are included.

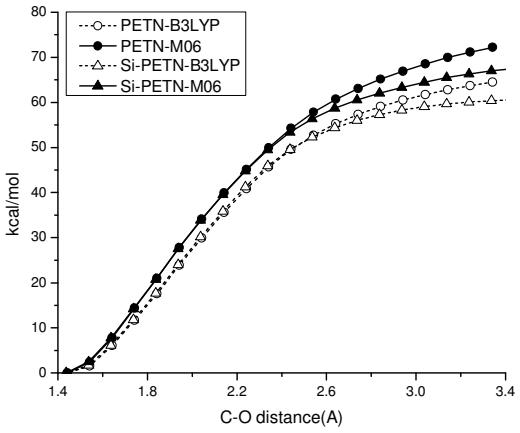

Figure S2. The C-O bond length scan by B3LYP and M06 at 6311G** level. Zero point energies are included

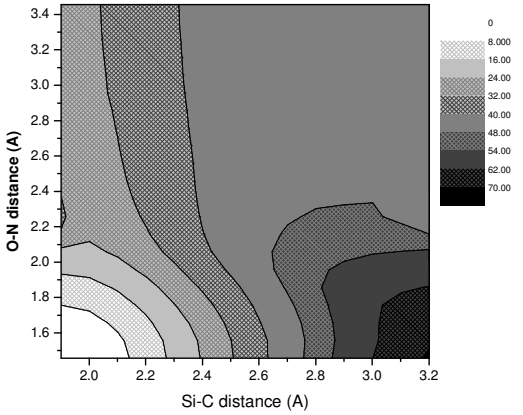

Figure S3. The two dimensional (Si-C and O-N bond) scan of Si-PETN by B3LYP at 6311G** level. The saddle point is taken at the bond distance of Si-C 2.701A and O-N 3.057A.

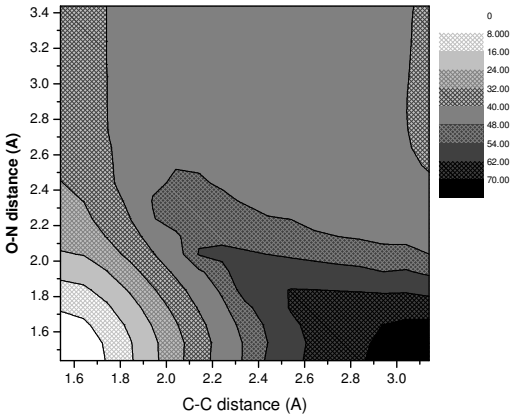

Figure S4. The two dimensional (C-C and O-N bond) scan of PETN by B3LYP at 6311G** level. The saddle point is taken at the bond distance of C-C 2.041A and O-N 2.839A

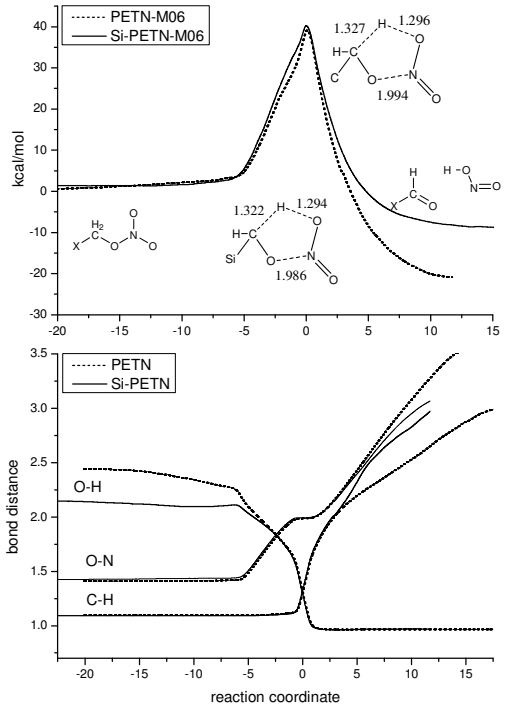

Figure S5. Energy and bond length vs. reaction coordinate of HONO dissociation (reaction 4) at M06/6311G** level. Zero point energy and thermal correction to 293.15K are included.

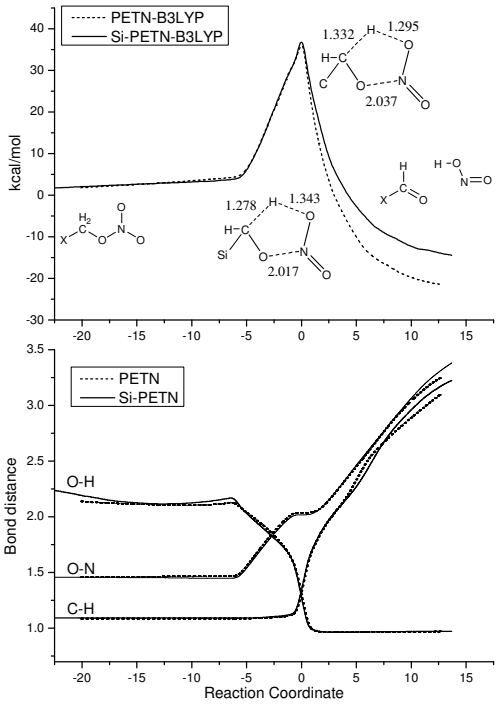

Figure S6. Energy and bond length vs. reaction coordinate of HONO dissociation (reaction 4) at B3LYP/6311G** level. Zero point energy and thermal correction to 293.15K are included

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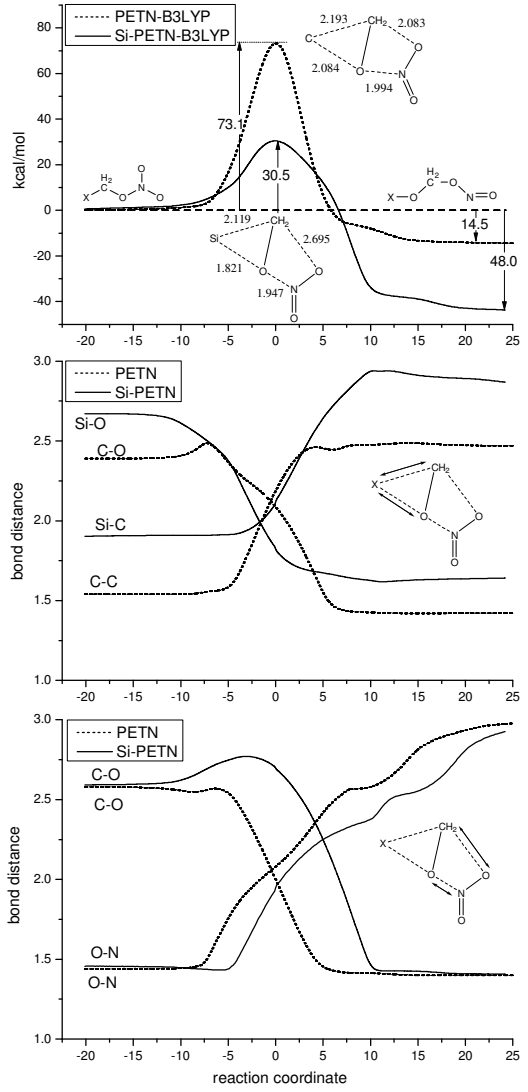

Figure S7. Energy and bond length vs. reaction coordinate of reaction 5 at B3LYP/6311G** level. Zero point energy and thermal correction to 293.15K are included.

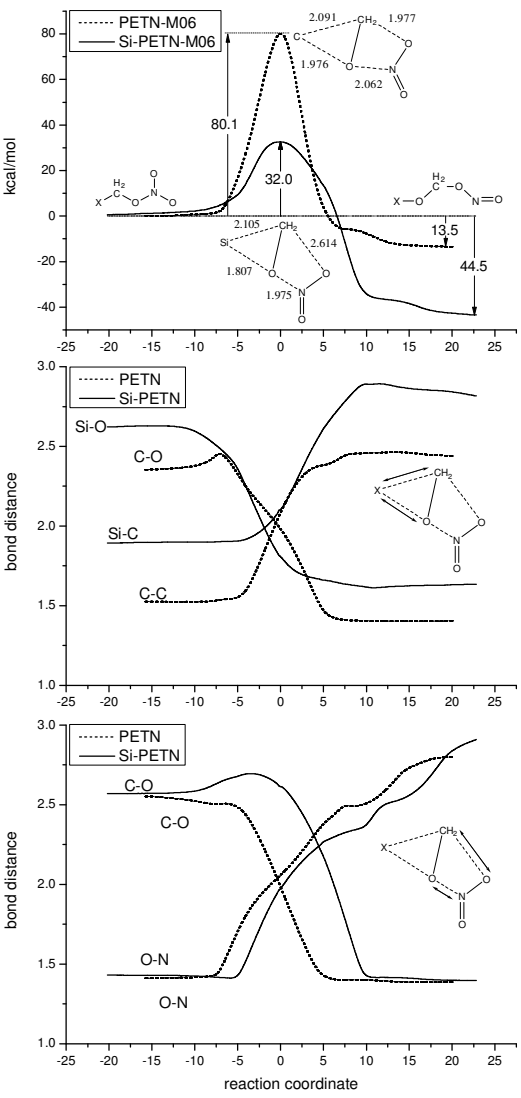

Figure S8. Energy and bond length vs. reaction coordinate of reaction 5 at M06/6311G** level. Zero point energy and thermal correction to 293.15K are included.

Table S2. The entropy and enthalpy change from ground state to transition state for reaction 4 and 5. Enthalpies are in kcal/mol and entropies are in cal/mol K. According to the transition state theory, $k_{uni}=kT/h*\exp(\Delta S/k)*\exp(-\Delta H/kT)$, where k is Boltzman constant, h is Planck constant and T is temperature. We conclude that for Si-PETN, reaction 5 is much faster than reaction 4.

	SiPETN			
Reaction	ΔS	ΔH	k_{uni}	ratio
4: HONO (TS)	0.1	39.4	8.0×10^{-17}	1
5: O-X (TS)	-5.6	32.0	1.3×10^{-12}	1.6×10^{4}

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